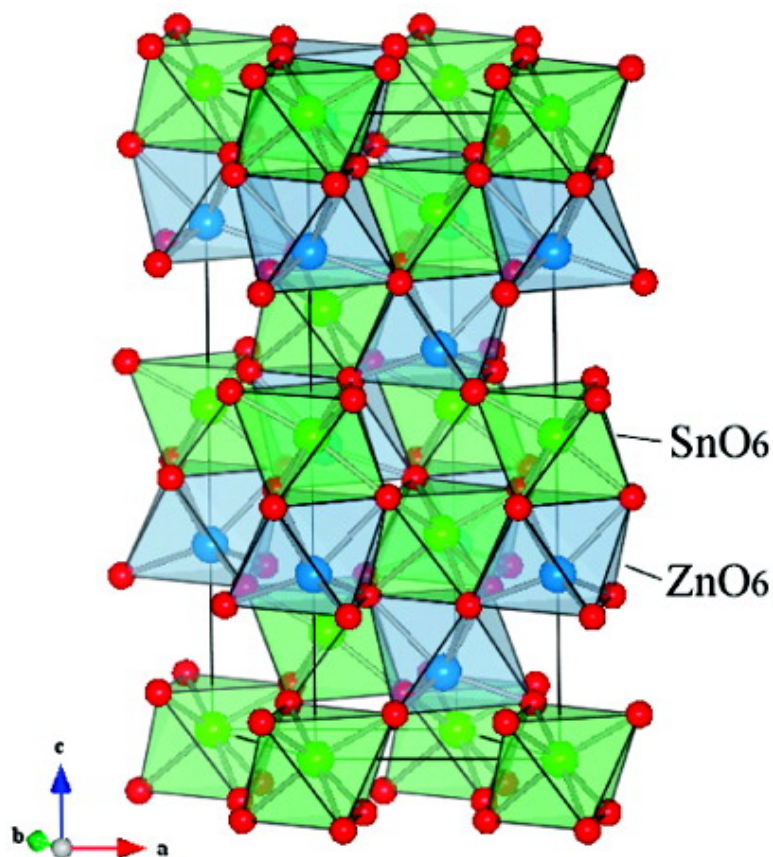


A Polar Oxide ZnSnO with a LiNbO-Type Structure

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A Polar Oxide ZnSnO₃ with a LiNbO₃-Type Structure

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Noncentrosymmetric (NCS) oxides, and especially the polar oxides among them, are of much interest in material science and engineering because their symmetry-dependent properties such as ferroelectricity, piezoelectricity, pyroelectricity, and second-order nonlinear optical behavior are technologically important.¹ In searching for polar oxides, much attention has been paid to oxides containing second-order Jahn–Teller distorted cations^{1–3} such as d⁰ transition metal ions (Ti⁴⁺, Nb⁵⁺, Ta⁵⁺, Mo⁶⁺, W⁶⁺, etc.) and cations with a lone pair electrons of ns² (Pb²⁺, Bi³⁺, etc.). In particular, since ferroelectric perovskites containing Pb²⁺ and Bi³⁺ exhibit high polarization and piezoelectric performance, the new Pb- and Bi-based perovskites^{4–12} have lately attracted considerable attention as candidate ferroelectric and multiferroic oxides. In contrast, little attention has been paid to oxides containing only main-group cations with the electronic configuration of (n–1)d¹⁰ns⁰, except for the polar wurzite-type ZnO.^{13,14} In this study, we have found that ZnSnO₃ with a LiNbO₃(LN)-type structure synthesized under high pressure is a polar crystal. This compound contains only the cations with the electronic configuration of (n–1)d¹⁰ns⁰, Zn²⁺, and Sn⁴⁺. While the high-pressure synthesis of LN-type oxides CuTaO₃,¹⁵ MnMO₃ (M = Ti,¹⁶ Sn^{17a}), and FeTiO₃¹⁷ have been reported, there has been no report on the LN-type ZnSnO₃.

Polycrystalline ZnSnO₃ was synthesized by a solid-state reaction under high pressure at elevated temperature. The mixture of stoichiometric amounts of ZnO and SnO₂ was allowed to react in a cubic multianvil-type high pressure apparatus at 7 GPa and 1000 °C for 30 min and then was quenched to room temperature. The experimental details about high-pressure synthesis are found as Supporting Information.

The phase was identified by the X-ray powder diffraction (XRD) method using a Rigaku RINT2100 diffractometer (graphite-monochromatized Cu Kα). The crystal structure of ZnSnO₃ was refined using the Rietveld analysis program, RIETAN 2000.¹⁸ The XRD data for refinement were collected in the range 2θ = 20–120° at 0.02° intervals at room temperature. Peak profiles were fitted with the pseudo-Voigt function. The color of the as-synthesized sample is gray. The XRD pattern of the as-synthesized sample showed the rhombohedral phase and small residual amounts of SnO₂, unknown phase, and a spinel-type Zn₂SnO₄. When the as-synthesized sample was annealed at 600 °C for 6 h and 700 °C for 6 h in air, the color turned to white. The XRD pattern of the rhombohedral ZnSnO₃ was unchanged after annealing. In contrast, the unknown phase and Zn₂SnO₄ were not detected after annealing (see Supporting Information, Figure S1). The gray color of the as-synthesized sample therefore originates from the unknown phase or a small number of oxygen vacancies. The unknown phase is probably a high-pressure phase and is decomposed into some other phases after annealing, though they were not found in the XRD pattern due to their small quantities. The XRD profile of the rhombohedral phase could be indexed with unit cell parameters, a = 0.52622(1) nm, c = 1.40026(2) nm. Reflection conditions derived from the indexing were –h + k + l = 3n for hkl, l = 2n for $\bar{h}h0l$, and l = 6n for

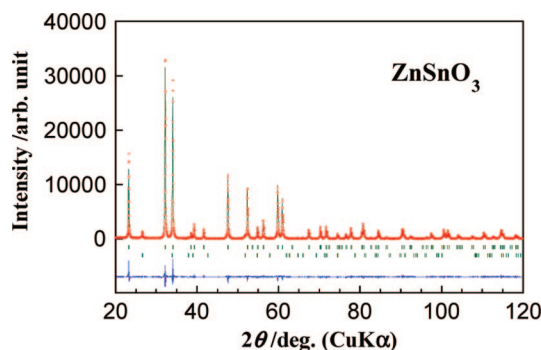


Figure 1. Observed (+) and calculated (solid line) X-ray powder diffraction patterns, difference (solid line on the bottom), and peak positions (l) of ZnSnO₃ and SnO₂.

Table 1. Structural Parameters in ZnSnO₃^a

atom	site	x	y	z	B/Å ²
Zn	6a	0	0	0.2859(1)	1.29(4)
Sn	6a	0	0	0	0.52(2)
O	18b	0.0405(8)	0.350(1)	0.0709(6)	0.43(8)

^a Hexagonal, space group *R3c* (No. 161), *Z* = 6, *a* = 0.52622(1) nm, *c* = 1.40026(2) nm; *R*_{wp} = 10.15%, *R*_p = 8.06%, *R*_e = 4.45%, *S* = 2.28, *R*_I = 2.84%, *R*_F = 2.32%.

00*l* (*n*: integer). Considering the reflection conditions, the possible space groups are the NCS *R3c* (No. 161) and the centrosymmetric *R3̄c* (No. 167). In the Rietveld refinements applying the space groups *R3c* and *R3̄c*, we obtained a much lower *R* factor (*R*_{wp} = 10.15%, *R*_I = 2.83%) when applying *R3c* than that (*R*_{wp} = 24.84%, *R*_I = 15.33%) with *R3̄c*. Furthermore, when the second harmonic generation (SHG) response of the annealed sample was tested in a reflection-geometry using YAG:Nd laser (λ = 1064 nm), the SHG signal could be detected, indicating that ZnSnO₃ is a NCS oxide. These results support that ZnSnO₃ crystallizes with NCS space group *R3c*. Since the corresponding point group 3*m* (*C*_{3*v*}) belongs to a polar crystal class, detection of the SHG signal is consistent with the structural symmetry. Figure 1 shows the observed and calculated XRD patterns and their differences. The scale factors for ZnSnO₃ and SnO₂ are 2.277(7) × 10^{−5} and 1.28(4) × 10^{−5}, respectively. Using the equation given by Bish and Howard,¹⁹ the amount of SnO₂ is estimated to be 2.5 wt % (3.8 mol %). The refined structural parameters for ZnSnO₃ are listed in Table 1.

The crystal structure is the same as that of a polar oxide LiNbO₃.^{20–22} Figure 2 shows the crystal structure of ZnSnO₃ from the perspective of an octahedra framework. Sn and Zn octahedra share both faces and edges with one another, each Sn octahedron shares corners with other Sn octahedra, and each Zn octahedron shares corners with other Zn octahedra. The cation sequence along the *c*-axis is Sn–Zn–Vac–Sn–Zn–Vac–Sn... (Vac = vacancy). The selected interatomic distances and the bond angles of ZnSnO₃ are listed in Table S1 of Supporting Information. The bond valence sums (BVS)²³ of

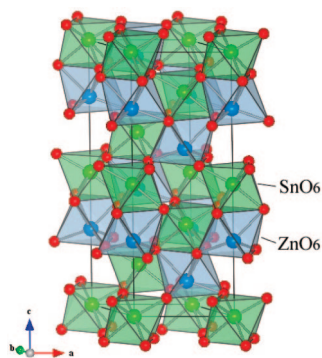


Figure 2. Crystal structure of ZnSnO₃.

Zn, Sn, and O are calculated to be 1.79, 4.08, and 1.96, respectively. The Zn–O bond is greatly under-bonded. The Sn–O distances in ZnSnO₃ are 0.2005 nm (×3) and 0.2094 nm (×3) and are slightly deviated from those of perovskite-type stannates with SnO₆ octahedra, CaSnO₃,²⁴ SrSnO₃,²⁴ and BaSnO₃²⁵ (0.2054–0.2066 nm). The distortion of Sn octahedron estimated by the equation,^{23a} $\Delta = 1/6\sum\{(d - d_{av})/d_{av}\}^2$, $\Delta_{Sn} = 5 \times 10^{-4}$, is somewhat smaller than $\Delta_{Li} = 18 \times 10^{-4}$ for LiO₆ and $\Delta_{Nb} = 40 \times 10^{-4}$ for NbO₆ in LiNbO₃. Here, d and d_{av} denote the individual interatomic distance and the average distance, respectively. In contrast, the two kinds of Zn–O distances are very different, 0.2041 nm (×3) and 0.2310 nm (×3) because the Zn ion is located in a greatly distorted position along the c -axis toward the vacant site, resulting in a large value of $\Delta_{Zn} = 38 \times 10^{-4}$. Therefore each Zn bonds to three oxygen atoms more covalently than the other three.

Since materials with the point group $3m$ (C_{3v}) also exhibit piezoelectricity and pyroelectricity, ZnSnO₃ is a candidate piezoelectric and pyroelectric material as well as a nonlinear optical material. Considering the symmetry, the polar axis is along the c -axis. The polarization, P , was estimated using the structural data according to the equation

$$P = \sum_i q_i \delta z_i / V$$

Here, q_i is the formal charge of each ion, δz_i is its displacement along the c -axis, and V is the unit cell volume. The summation is performed over all ions in the unit cell. The calculated value is $P = 59 \mu\text{C}/\text{cm}^2$, which is compared to the calculated value of $67 \mu\text{C}/\text{cm}^2$ for LiNbO₃²² and is much greater than that of $5 \mu\text{C}/\text{cm}^2$ for ZnO.¹³ The large spontaneous polarization primarily originates from displacement of the Zn ion based on the peculiar chemical bonding between Zn and O as mentioned above.

The solid-state reaction between ZnO and SnO₂ in the pressure range from ambient pressure to 5 GPa gives neither LiNbO₃(LN)-type ZnSnO₃ nor ilmenite (IL)-type ZnSnO₃, resulting in a mixture of spinel-type Zn₂SnO₄ and rutile-type SnO₂ (see Supporting Information, Figure S2). Kovacheva and Petrov²⁶ have reported that the IL-type ZnSnO₃ ($R\bar{3}$, $a = 0.528$ nm, $c = 1.409$ nm, $Z = 6$) can be obtained by an ion-exchange reaction between α -Li₂SnO₃ and a melt of ZnCl₂–KCl. Furthermore, we confirmed that the LN-type ZnSnO₃ is stable up to 700 °C and is partially decomposed into the spinel-type Zn₂SnO₄ and the rutile-type SnO₂ at 800 °C at ambient atmosphere (see Supporting Information, Figure S3). The smaller molar volume of LN-type ZnSnO₃ (55.97 Å³) than that of (1/2 Zn₂SnO₄²⁷ + 1/2 SnO₂²⁸) (58.3 Å³) is consistent with the fact that the LN-type ZnSnO₃ is the high-pressure form. In contrast, the ilmenite structure is not the thermodynamically favored form at any pressure though the molar volumes of IL-type ZnSnO₃²⁶

(56.78 Å³) is smaller than that of (1/2 Zn₂SnO₄ + 1/2 SnO₂) and greater than that of LN-type ZnSnO₃.

In this study a novel polar LiNbO₃-type oxide ZnSnO₃ was obtained by high-pressure synthesis. The polar structure is primarily characterized by a large displacement of Zn based on strong covalent bonding between Zn and three O. The finding of a polar ZnSnO₃ containing only cations with an electronic configuration of $(n-1)d^{10}ns^0$ gave us a new strategy in searching for polar crystals.

Acknowledgment. The authors thank Professor Yoshiaki Uesu and Mr. Yuuichi Mashita of Waseda University for performing the second harmonic generation test. This work was supported by the “High-Technology Research Center Project” of the MEXT of Japan. Figure 2 was drawn with the computer program VICS developed by Dr. R. A. Dilanian and Dr. F. Izumi.

Supporting Information Available: Experimental details regarding high-pressure synthesis of ZnSnO₃. The XRD patterns for as-synthesized and annealed samples of ZnSnO₃. The selected interatomic distances and bond lengths of ZnSnO₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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